EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

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Exhibit D - Analytical Methods for Semivolatiles

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1.0 SCOPE AND APPLICATION

1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of semivolatiles in hazardous waste samples. These methods were based on USEPA Method 625, Base/Neutral and Acids. In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis for other USEPA methods to perform the analysis of semivolatiles contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of semivolatiles at hazardous waste sites.

1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites for the semivolatile organic compounds on the Target Compound List (TCL) [see Exhibit C (Semivolatiles)]. It covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to Gas Chromatography (GC). The method involves solvent extraction of the matrix sample, characterization to determine the appropriate analytical protocol to be used, followed by appropriate cleanup procedure and GC/Mass Spectrometry (MS) analysis to determine the semivolatile organic compounds present in the sample. In addition, if requested, sample extracts will be analyzed for a select group of compounds, including Polynuclear Aromatic Hydrocarbons (PAHs) and pentachlorophenol by GC/MS, using the Selected Ion Monitoring (SIM) technique. If a SIM analysis is requested, a full scan analysis using the low-level method should be performed <u>first</u>. If all PAHs and pentachlorophenol are detected during the full scan analysis using the low-level method, then a SIM analysis is not to be performed and this should be documented in the SDG Narrative.

1.3 This analytical method provides the use of SW-846 Methods 3520C (Revision 3, December 1996); 3541 (Revision 0, September 1994); 3545A (Revision 1, January 1998); and 3550C (Revision 3, November 2000) for the extraction of soil/sediment samples. The method includes the use of Deuterated Monitoring Compounds (DMCs) for precision and accuracy assessment.

1.4 Problems have been associated with the following compounds analyzed by this method.

1.4.1 Dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration.

1.4.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the GC inlet, chemical reactions in acetone solution, and photochemical decomposition.

1.4.3 N-nitrosodiphenylamine decomposes in the GC inlet forming diphenylamine and consequently, may be detected as diphenylamine.

2.0 SUMMARY OF METHOD

2.1 Water

A 1 L aliquot of sample is acidified to pH 2.0, mixed with Deuterated Monitoring Compounds (DMCs), and extracted with methylene chloride using a continuous liquid-liquid extractor. Separatory funnel extraction is NOT permitted. The methylene chloride extract is dried with sodium sulfate (or an equivalent drying agent such as Hydromatrix™), concentrated, subjected to Gel Permeation Chromatography (GPC) (GPC is required when higher molecular weight compounds are present that interfere with the analyses of target compounds; GPC is optional for all other circumstances), and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for extractable organics.

2.2 Low-Level Soil/Sediment

A 30 g portion of soil/sediment is mixed with anhydrous powdered sodium sulfate (or Hydromatrix) and DMCs, and extracted with 1:1 methylene chloride/acetone solution using an ultrasonic probe, a Soxhlet extractor, or a pressurized fluid extractor. The extract is concentrated, subjected to GPC cleanup, and analyzed by GC/MS for extractable organics.

The Contractor must determine whether a soil/sediment sample should be analyzed by the low-level or medium-level method, using a USEPA-approved screening procedure or an in-house laboratory screening procedure.

2.3 Medium-Level Soil/Sediment

Approximately 1 g portion of soil/sediment is mixed with anhydrous powdered sodium sulfate (or Hydromatrix) and DMCs in a vial and extracted with methylene chloride. The methylene chloride extract is subjected to GPC cleanup and optional silica gel cleanup (SW-846 Method 3630C), prior to analysis by GC/MS for extractable organics.

2.4 Internal standards are added to all samples, standards, requested Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and blanks. The target compounds and DMCs are identified in the samples and blanks by analyzing standards that contain all target compounds, DMCs, and internal standards under the same conditions and comparing resultant mass spectra and GC Retention Times (RTs). A Relative Response Factor (RRF) is established for each target compound and DMC during the initial and continuing calibrations by comparing the mass spectra response from the Extracted Ion Current Profile (EICP) for the primary quantitation ion produced by that compound to the mass spectra response for the primary quantitation ion produced by the associated internal standard compound. Each identified target compound and DMC is quantitated by comparing the instrument response for the compound in the sample, standard, requested MS/MSD, or blank with the instrument response of the associated internal standard, while taking into account the Mean RRF ($\overline{RRF}$) from the most recent initial calibration, the sample weight/volume, the moisture content of soil samples, and any sample dilutions.

2.5 Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library. Non-target compounds are quantitated by comparing the mass spectra response from the Reconstructed Ion Chromatogram (RIC) for the non-target compound peaks to the mass spectra response produced by the nearest internal standard. An RRF of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the Extracted Ion Current Profiles (EICPs). All of the materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety & Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analyses.

5.2 Specifically, concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors - Equipped with polytetrafluoroethylene (PTFE) or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.1.2 Beakers - 400 mL.

6.1.3 Syringes - 2 µL, 10 µL, 0.1 mL, 0.2 mL, 0.5 mL. 1 mL, 5 mL, and 10 mL with Luer-lok fitting.

6.1.4 Glass Scintillation Vials - At least 20 mL with screw-cap and PTFE or aluminum foil liner.

6.1.5 Pasteur Pipets - 1 mL glass, disposable.

6.1.6 Vial and Caps - Amber glass, 2 mL capacity with PTFE-lined screw-cap, 2 mL capacity for Gas Chromatograph (GC) auto sampler.

Vials for collection of extracts - 40 mL or 60 mL, pre-cleaned, open top screw-cap with PTFE-lined silicone septum.

6.1.7 Drying Column - 19 mm ID chromatographic column with coarse frit (substitution of a small pad of borosilicate glass wool for the frit will help prevent cross contamination of sample extracts).

6.1.8 Class A Graduated Cylinder - 100 mL.

6.1.9 Class A Volumetric Flasks - 10 mL.

6.2 Kuderna-Danish (K-D) Apparatus

6.2.1 Concentrator Tubes - 15 mL and 10 mL graduated. Calibration must be checked at the volumes employed in the test. Ground-glass stoppers are used to prevent evaporation of extracts.

6.2.2 Evaporative Flasks - 500 mL. Attach to concentrator tube with springs.

6.2.3 Snyder Column - Three-ball macro.

6.2.4 Snyder Column - Two-ball micro.

6.3 Spatula - Stainless steel or PTFE.

6.4 Balances - Analytical, capable of accurately weighing ±0.0001 g, and one capable of weighing 100 g (±0.01 g). The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with Class S weights at a minimum of once per month. The balances must also be checked annually by a certified technician.

6.5 Ultrasonic Cell Disrupters - 300 watt with pulsing capability, ½ inch tapered disrupter horn, 1/8 inch standard tapered microtip probe, and 3/4 inch tapered high gain "Q" disrupter horn, or 3/4 inch standard solid disrupter horn.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the microtip probe or horn shall be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

6.6 Sonabox Acoustic Enclosure (or equivalent) - For use with disrupter to decrease noise level.

6.7 Pressurized Fluid Extraction Device - Dionex Accelerated Solvent Extractor (ASE-300) or equivalent with appropriately sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure environments (2000+ psi) necessary for this procedure.

6.7.1 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.8 Automated Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil must not be used because it destroys the rubber parts. The apparatus must be used in a hood.

6.8.1 Cellulose or Glass Extraction Thimble - 26 mm ID x 60 mm.

6.8.2 Glass Extraction Cups.

6.8.3 Thimble Adapters.

6.8.4 Viton Seals.

6.9 Vacuum Filtration Apparatus

6.9.1 Buchner Funnel.

6.9.2 Filter Paper - Whatman No. 41 or equivalent.

6.10 Borosilicate Glass Wool - Rinsed with methylene chloride.

6.11 Test Tube Rack

6.12 Silicon Carbide Boiling Chips - Approximately 10/40 mesh. Heat to 400°C for 30 min. or Soxhlet extract with methylene chloride. PTFE boiling chips solvent rinsed prior to use are acceptable.

6.13 Water Bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

6.14 Oven - Drying.

6.15 Desiccator.

6.16 Crucibles - Porcelain.

6.17 Nitrogen Evaporation Device - Equipped with a water bath that can be maintained at 35-40°C. To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device must be used in a hood.

6.18 pH Paper - Including narrow range capable of measuring a pH of 2.0.

6.19 pH Meter - With a combination glass electrode. Calibrate according to manufacturer's instructions. The pH meter shall be calibrated prior to each use.

6.20 Gel Permeation Chromatography (GPC) Cleanup System

6.20.1 GPC System - Systems that perform satisfactorily have been assembled from the following components - a High Performance Liquid Chromatograph (HPLC) pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 10.3.3.

NOTE: GPC cleanup is required for all soil/sediment extracts, and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target compounds.

6.20.2 Chromatographic Column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.20.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect the inlet side of the analytical column.

6.20.4 Bio Beads (SX-3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads are required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.20.5 Ultraviolet Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.20.6 Strip Chart Recorder, recording integrator, or laboratory data system.

6.20.7 Syringe Filter Assembly disposable - 5 micron filter discs.

NOTE: Consult the instrument operation manual to determine the proper filter disc to use in the system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.21 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.21.1 Gas Chromatograph - The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout the temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.21.2 Gas Chromatography Column - Minimum length 30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicon coated fused silica capillary column DB-5 (J&W Scientific); RTX-5, RTX-5 Sil Ms (Restek); Zebron ZB-5 (Phenomenex); SPB-5 (Supelco); AT-5 (Alltech); HP-5 (Agilent); CP-Sil 8CB (Chrompack); 007-2 (Quadrex); BP-5 (SGE); or equivalent. Note that this is a minimum requirement for column length. Longer columns may be used. Although a film thickness of 1.0 micron is recommended because of its larger capacity, a film thickness of 0.25 micron may be used. A description of the GC column used for analysis shall be provided in the SDG Narrative.

6.21.2.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantification of the compounds listed in Exhibit C (Semivolatiles).
- The analytical results generated using the column meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method, and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Semivolatiles).
- The column can accept up to 160 ng of each compound listed in Exhibit C (Semivolatiles), without becoming overloaded.
- The column provides equal or better resolution of the compounds listed in Exhibit C (Semivolatiles), than columns listed in Section 6.21.2.

6.21.2.2 As applicable, follow the manufacturer's instructions for use of its product.

6.21.2.3 The Contractor must maintain documentation that the column met the criteria in Section 6.21.2.1. The minimum documentation is as follows:

6.21.2.3.1 Manufacturer provided information concerning the performance characteristics of the column.

6.21.2.3.2 Reconstructed ion chromatograms and data system reports generated on the GC/MS used for Contract Laboratory Program (CLP) analyses:

- From blanks that demonstrate that there are no contaminants that interfere with the semivolatile analysis when using the column.
- For initial calibration standards analyzed using the column.
- For Continuing Calibration Verification (CCV) standards analyzed using the column.

6.21.2.3.3 Based on the Contractor-generated data described in Section 6.21.2.3.2, the Contractor must complete a written review, signed by the Laboratory Manager, certifying that:

- The column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5.

- The low-point initial calibration standard analysis has adequate sensitivity to meet the semivolatile CRQLs.
- The high-point initial calibration standard analysis was not overloaded.
- The column does not introduce contaminants that interfere with the identification and/or quantitation of compounds listed in Exhibit C (Semivolatiles).

6.21.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request by the USEPA Regional CLP Project Officer (CLP PO).

6.21.2.5 **PACKED COLUMNS CANNOT BE USED.**

6.21.3 Mass Spectrometer

Must be capable of scanning from 35-500 amu every 1 sec. or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum that meets the tuning acceptance criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. The system must be capable of Selected Ion Monitoring (SIM). The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.21.4 GC/MS Interface

The Contractor may use any GC/MS interface that provides acceptable sensitivity at CRQLs. However, direct insertion of the GC column into the Mass Spectrometer source is the recommended interface. GC/MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.21.5 Data System

A computer system interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library shall be used as the reference library. The operational data system must be capable of and is required to flag all data files that have been edited manually by laboratory personnel.

6.21.6 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent Water - Reagent water is defined as water in which an interferent is not observed at or above the Contract Required Quantitation Limit (CRQL) for each analyte of interest. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.2 Sulfuric Acid Solution (H_2SO_4) - (1+1) slowly add 50 mL of concentrated H_2SO_4 (sp. gr. 1.84; 18 N) to 50 mL of reagent water.

7.1.3 Acetone, methanol, methylene chloride, iso-octane, 2-propanol, and toluene - pesticide residue analysis grade or equivalent.

7.1.4 Sodium Sulfate - Powdered or granular anhydrous reagent grade, heated at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

OR

Hydromatrix - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 7. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from preparation date. The expiration date of the ampulated standards, upon the breaking of the glass seal, is 6 months (or sooner, if the standard has degraded or evaporated).

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be purchased or prepared in methylene chloride or another suitable solvent.

7.2.3 Working Standards

7.2.3.1 Deuterated Monitoring Compound (DMC) Standard Spiking Solution

7.2.3.1.1 Prepare a DMC standard spiking solution in methanol to contain the following compounds shown:

DMC

Phenol-d_5

Bis-(2-chloroethyl)ether-d_8

2-Chlorophenol-d_4

4-Methylphenol-d_8

Nitrobenzene-d_5

2-Nitrophenol-d_4

2,4-Dichlorophenol-d_3

4-Chloroaniline-d_4

Dimethylphthalate-d_6

Acenaphthylene-d_8

4-Nitrophenol-d_4

Fluorene-d_{10}

4,6-Dinitro-methylphenol-d_2

Anthracene-d_{10}

Pyrene-d_{10}

Benzo(a)pyrene-d_{12}

Fluoranthene-d_{10} [Selected Ion Monitoring (SIM) analysis]

2-Methylnapthalene-d_{10} (SIM analysis)

7.2.3.1.2 DMC standards are added to all samples, blanks, requested Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and calibration solutions. The SIM compounds can be added as part of the DMC standard spiking solution or added separately to all standards, samples, and blanks that require SIM analysis. The DMC standard spiking solution must be prepared every 12 months, or sooner if the solution has degraded or concentrated.

7.2.3.2 Matrix Spiking Solution

7.2.3.2.1 The matrix spiking solution consists of the following:

Bases/Neutrals	Acids
Acenaphthene	Pentachlorophenol
2,4-Dinitrotoluene	Phenol
Pyrene	2-Chlorophenol
N-Nitroso-di-n-propylamine	4-Chloro-3-methylphenol
	4-Nitrophenol

7.2.3.2.2 Prepare a spiking solution that contains each of the base/neutral and acid compounds listed above in methanol (see Section 12.2.3 for appropriate concentrations).

7.2.3.2.3 For SIM analyses, the laboratory has the option of using the matrix spiking solution in Section 7.2.3.2.1 or preparing a matrix spiking solution containing only acenaphthene, pyrene, and pentachlorophenol in methanol (see Section 12.2.3 for appropriate concentrations).

7.2.3.3 Gel Permeation Chromatography (GPC) Calibration and GPC Continuing Calibration Verification Solution

7.2.3.3.1 Prepare a calibration solution in methylene chloride containing the following analytes at the minimum concentration listed (in elution order):

Compound	Concentration (mg/mL)
Corn oil	25.0
Bis(2-ethylhexyl)phthalate	0.5
Methoxychlor	0.1
Perylene (CAS # 198-55-0)	0.02
Sulfur (CAS # 7704-34-9)	0.08

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.3.4 Instrument Performance Check Solution

Prepare a solution containing decafluorotriphenylphosphine (DFTPP) in methylene chloride. The solution may be incorporated into the calibration standard used as the mid-level initial calibration standard and the continuing calibration standard verification standard, or may be prepared as a single analyte solution. If DFTPP is incorporated into the calibration standard, then an aliquot of the DFTPP solution is to be added to the autosampler vial containing either the initial calibration mid-level standard, or Continuing Calibration Verification (CCV) before calibration analysis. The DFTPP must be analyzed using the same Gas Chromatograph (GC) and Mass Spectrometer run conditions as is used for the calibration analysis. The DFTPP solutions are to be prepared such that 50 ng of DFTPP is injected onto the column.

7.2.3.5 Initial and Continuing Calibration Solutions

7.2.3.5.1 Calibration standards are to be prepared at a minimum of five concentration levels in methylene chloride at concentrations that are applicable to the sensitivity of the instrument. For most operations, the calibrations standards are to be prepared at 5.0, 10, 20, 40 and 80 ng/µL for each target compound and associated DMCs (see Table 7). These levels are based upon 1.0 mL final volume extracts for samples not undergoing GPC cleanup, and 0.5 mL final volume extracts for those samples undergoing GPC cleanup. Other concentration levels may be used for more sensitive instrumentation and final extract levels. For example, a laboratory may use a final extract volume of 1.0 mL for samples undergoing GPC cleanup, and a low calibration standard of 2.5 ng/µL. The alternate calibration

standards and final volumes may be used as long as the following requirements are met:

(a) The laboratory can demonstrate that the CRQL for each analyte listed in Exhibit C can be reached using the calibration and final volume scheme. This demonstration is made when there is formal documentation of laboratory Method Detection Limit (MDL) studies indicating that the calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final volume and calibration level scheme.

(b) All five calibration levels are in the same ratio as that shown above (e.g., if a lab were using a 1.0 ng/µL low standard, then the other calibration levels must be 2.0, 4.0, 8.0, and 16 ng/µL).

Each calibration standard should contain each target compound. Each DMC may be added to the other calibration standards, or may be contained in a separate mixture and combined with the calibration standards in the autosampler vials just prior to analysis. Seven compounds (2,4-Dinitrophenol, Pentachlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, and 4,6-Dinitro-2-methylphenol) will require only a four-point initial calibration at 10, 20, 40, and 80 ng/µL since detection at less than 10 ng/µL is difficult. The USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Organic Program Manager (PM) has the authority to disallow certain alternative calibration standard concentrations or final extract volume schemes if it is felt that it is inappropriate or that it may lead to questionable data.

NOTE: 1.0 or 2.0 µL injections of all calibration standards may be used. All samples analyzed must have been injected at the same volume (1.0 or 2.0 µL) as the calibration standard.

7.2.3.5.2 If the optional analysis of Polynuclear Aromatic Hydrocarbons (PAHs) and pentachlorophenol using the Selected Ion Monitoring (SIM) technique is to be performed, prepare calibration standards at a minimum of five concentration levels that are applicable to the sensitivity of the instrument. For most operations, the calibrations standards are to be prepared at 0.10, 0.20, 0.40, 0.80, and 1.0 ng/µL for each target compound of interest and the associated DMCs (see Table 8). Pentachlorophenol will require only a four-point initial calibration at 0.20, 0.40, 0.80, and 1.0 ng/µL.

NOTE: 1.0 or 2.0 µL injections of all calibration standards may be used. All samples analyzed must have been injected at the same volume (1.0 or 2.0 µL) as the calibration standard.

7.2.3.5.3 The CCV standard should be at or near the mid-point concentration level of the calibration standards, normally 20 ng/µL. If the optional analysis of PAHs/pentachlorophenol by SIM is to be performed, the CCV standard should be at or near the mid-point calibration level, normally 0.40 ng/µL.

7.2.3.5.4 To facilitate the confirmation of single component pesticides from the semivolatile library search data [see Exhibit D

(Pesticides), Section 11.1.2], the laboratory may include the single component pesticide target compounds listed in Exhibit C (Pesticides), Section 3.0, in the semivolatile CCV standard. The laboratory may add any or all of these compounds to the semivolatile CCV standard, but at a concentration of 10 ng/µL or less. Do not include the Aroclor or Toxaphene mixtures in the semivolatile initial and continuing calibration verification standards. If added to this Gas Chromatograph/Mass Spectrometer (GC/MS) standard, these additional analytes are not reported on the semivolatile calibration form (Form VII), but must be included in the quantitation report for the CCV standard. As only a single point calibration would be performed, no Percent Relative Standard Deviation (%RSD) or Percent Difference (%Difference) criteria would apply to these additional analytes.

7.2.3.6 Internal Standard Solution

7.2.3.6.1 Prepare an internal standard solution containing each of the following compounds in methylene chloride: 1,4-dichlorobenzene-d_4; naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; and perylene-d_{12}. It may be necessary to use 5-10% toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. Just prior to full scan analysis by GC/MS, add sufficient amount of the internal standard solution to an aliquot of the water, low-level, or medium-level soil sample extract to result in a 20 ng/µL concentration of each internal standard.

7.2.3.6.2 If the optional analysis of PAHs/pentachlorophenol by SIM is to be performed, just prior to SIM analysis the Contractor shall add sufficient amount of the internal standard solution to an aliquot of the water or low-level sample extract to result in a 0.40 ng/µL concentration of each internal standard. 1,4-dichlorobenzene-d_4 is not required to be evaluated as an internal standard when performing SIM analysis.

7.3 Storage of Standard Solutions

7.3.1 Store the stock standard solutions at 4°C (±2°C) in polytetrafluoroethylene (PTFE)-lined screw-cap amber bottles. Fresh standards should be prepared every 12 months at a minimum.

7.3.2 Store the working standards at 4°C (±2°C) in PTFE-sealed containers. The solution should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with Quality Control (QC) check samples indicates a problem.

7.3.3 The CCV standard should be stored at 4°C (±2°C). The solution should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with Quality Control (QC) check samples indicates a problem.

7.3.4 Refrigeration of the GPC calibration solution may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves. Replace this calibration solution every 6 months, or more frequently if necessary.

7.3.5 Protect all standards from light. Samples, sample extracts, and standards must be stored separately.

7.3.6 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means, at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with polytetrafluoroethylene (PTFE)-lined screw-caps. If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed-end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the Region.

8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery of a complete, reconciled data package to USEPA.

8.3.2 Samples, sample extracts, and standards must be stored separately.

8.4 Contract Required Holding Times

8.4.1 Extraction of water samples shall be started within 5 days of Validated Time of Sample Receipt (VTSR). Extraction of soil/sediment samples shall be completed within 10 days of VTSR.

8.4.2 As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples as standard extracts that the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the Sample Delivery Group (SDG). The extraction holding time (5 days after VTSR for water and 10 days after VTSR for soil/sediment) does not apply to PE samples received as standard extracts.

8.4.3 Extracts of water and soil/sediment samples must be analyzed within 40 days following extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Gas Chromatograph (GC)

9.1.1.1 The following are only suggested gas chromatographic analytical conditions. Other conditions may be used, provided that all technical acceptance criteria in Sections 9.3.5, 9.4.5, and 11.3 are met. For example, newer columns that are stable at temperatures of up to 370°C may be used. The use of these columns would decrease run time while still providing adequate resolution.

Initial Column Temperature Hold	40°C for 4 min.
Column Temperature Program	40-270°C at 10°C/min.
Final Column Temperature Hold	270°C; Hold Required: 3 min. after all compounds listed in Exhibit C (Semivolatiles), have eluted
Injector Temperature	250-300°C
Transfer Line Temperature	250-300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, splitless
Sample Volume	1 or 2 µL
Carrier Gas	Helium at 30 cm/sec.

9.1.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and Matrix Spike and Matrix Spike Duplicates (MS/MSDs).

9.1.2 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy	70 volts (nominal)
Mass Range	35 to 500 amu
Ionization Mode	Electron Ionization (EI)
Scan Time	Not to exceed 1 sec. per scan

NOTE: For SIM analyses the laboratory is to use professional judgment and the instrument manufacturer's instructions and guidelines in choosing an appropriate single ion scan or dwell time (usually 50 to 500 msec per ion).

9.2 GC/MS Mass Calibration (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Instrument Performance Check

The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibration such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.3.4). Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing decafluorotriphenylphosphine (DFTPP).

NOTE: The requirement to analyze the instrument performance check solution does not apply when the optional analysis of Polyaromatic Hydrocarbons (PAHs)/pentachlorophenol is to be performed.

9.2.2 Frequency of GC/MS Instrument Performance Check

9.2.2.1 The instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which samples or standards are analyzed. However, in cases where a closing Continuing Calibration Verification (CCV) can be used as an opening CCV for the next 12-hour time period, then an additional DFTPP tune is not required and the 12-hour time period begins with the injection of the CCV.

9.2.2.2 The 12-hour time period for a GC/MS system instrument performance check and calibration standards (initial or continuing calibration verification criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a closing CCV can be used as an opening CCV for the next 12-hour period, then an additional DFTPP tune is not required, and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

NOTE: For the optional analysis of PAHs/pentachlorophenol by the Selected Ion Monitoring technique (SIM), the 12-hour time period begins at the moment of injection of the first initial calibration standard or at the moment of injection of the CCV standard, if initial calibration is not to be performed. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the instrument performance check solution may be performed as an injection of 50 ng of DFTPP into the GC/MS or by adding a sufficient amount of DFTPP to the calibration standards to result in an on-column amount of 50 ng of DFTPP (Section 7.2.3.4) and analyzing the calibration standard.

9.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

9.2.4.1 The GC/MS system must be tuned at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Table 1 must be met for a 50 ng injection of DFTPP. The mass spectrum of DFTPP must be acquired in the following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Do not subtract part of the DFTPP peak.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical GC/MS instrument run conditions.

9.2.5 Corrective Action for GC/MS Instrument Performance Check

9.2.5.1 If the GC/MS instrument performance check technical acceptance criteria are not met, re-tune the GC/MS system. It may be necessary to clean the ion source, clean quadrupoles, or take other actions to achieve the technical acceptance criteria.

9.2.5.2 The instrument performance check technical acceptance criteria MUST be met before any standards, samples, including MS/MSDs, or required blanks are analyzed. Any standards, samples, or required blanks analyzed when the instrument performance check technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks, and after the instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.3.5.1) to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target and Deuterated Monitoring Compounds (DMCs). Each initial calibration standard contains all the semivolatile target compounds, DMCs, and internal standards.

NOTE: For optional analysis of PAHs/pentachlorophenol using the SIM technique, the GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.3.5.2), prior to the analysis of samples and required blanks, to determine instrument sensitivity and linearity. The calibration standards contain all the PAHs and pentachlorophenol, the associated DMCs, and internal standards.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be initially calibrated upon award of the contract, whenever the Contractor takes corrective action that may change or affect the initial calibration criteria (e.g., ion source cleaning or repairs, column replacement, etc.), or if the CCV technical acceptance criteria have not been met.

9.3.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period.

9.3.3 Procedure for Initial Calibration

9.3.3.1 All standard/spiking solutions and blanks must be allowed to warm to ambient temperature before preparation or analysis.

9.3.3.2 Prepare five calibration standards containing all the semivolatile target and DMCs at the concentrations described in Section 7.2.3.5.

9.3.3.3 Add sufficient amount of internal standard solution (Section 7.2.3.6) to aliquots of calibration standards to result in a 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.3.6 should permit most of the semivolatile target compounds to have Relative Retention Times (RRTs) of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

9.3.3.4 Analyze each calibration standard by injecting 1.0 or 2.0 µL of standard.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the Relative Response Factors (RRFs) for each semivolatile target and DMC using Equation 1 and the primary characteristic ions found in Table 3. Assign the target compounds and DMCs to the internal standard according to Table 2. For internal standards, use the primary ion listed in Table 3 unless interferences are present. If interferences prevent the use of the primary ion for a given internal standards, use the secondary ion(s) listed in Table 3.

NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 1 Relative Response Factor Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of the characteristic ion for the compound to be measured (Table 3).

A_{is} = Area of the characteristic ion for specific internal standard (Table 3).

C_{is} = Amount of the internal standard injected (ng).

C_x = Amount of the target compound or DMC injected (ng).

9.3.4.2 The Mean Relative Response Factor ($\overline{RRF}$) must be calculated for all compounds. Calculate the Percent Relative Standard Deviation (%RSD) of the RRF values for the initial calibration using Equation 2.

EQ. 2 Percent Relative Standard Deviation Calculation

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n-1}}$$

Where,

X_i = Each individual value used to calculate the mean.

$\overline{X}$ = The mean of n values.

n = The total number of values.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.3.5.1 and at the frequency described in Section 9.3.2 on a GC/MS system meeting the instrument performance technical acceptance criteria.

NOTE: All initial calibration standards for the optional analysis of PAHs/pentachlorophenol by the SIM technique must be analyzed at the concentration levels described in Section 7.2.3.5.2 and at the frequency described in Section 9.3.2.

9.3.5.2 The RRF at each calibration concentration for each semivolatile target compound and DMC must be greater than or equal to the compound's minimum acceptable RRF listed in Table 4.

9.3.5.3 The %RSD of the RRFs over the initial calibration range for each semivolatile target compound and DMC that has a required %RSD must be less than or equal to the %RSD listed in Table 4.

9.3.5.4 Up to four compounds may fail to meet the criteria listed in Sections 9.3.5.2 and 9.3.5.3. However, these four compounds must meet a minimum RRF criterion of 0.010 and have a %RSD less than or equal to 40%.

9.3.5.5 For the optional analysis of PAHs/pentachlorophenol using SIM technique, two compounds may fail to meet the criteria listed in Sections 9.3.5.2 and 9.3.5.3. However, those two compounds must meet a minimum RRF criterion of 0.010 and have a %RSD less than or equal to 40%.

9.3.5.6 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If any technical acceptance criteria for initial calibration are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria must be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Opening and Closing Continuing Calibration Verification

Prior to the analysis of samples and required blanks and after instrument performance check technical acceptance criteria and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a CCV standard (opening CCV) to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. The CCV standard contains all the semivolatile target compounds, DMCs, and internal standards. After all samples and blanks have been analyzed, and before the end of the 12-hour time period, a closing CCV using the same standard as for the opening CCV is required. The same injection volume must be used for all standards, samples, and blanks.

NOTE: For the optional analysis of PAHs/pentachlorophenol using SIM, each GC/MS system must be routinely checked by analyzing a CCV standard (opening CCV), prior to the analysis of samples and required blanks, and after initial calibration technical acceptance criteria have been met. The continuing calibration standard for optional analysis of PAHs/pentachlorophenol contains the PAHs and pentachlorophenol, the associated DMCs, and internal standards. After all samples and blanks have been analyzed, and before the end of the 12-hour time period, a closing CCV using the same standard conditions as for the opening CCV is required.

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 Each GC/MS used for analysis must be calibrated once every 12-hour time period of operation. The 12-hour time period begins with the injection of DFTPP for full scan analysis followed by the injection of the opening CCV. If a closing CCV meets the technical acceptance criteria for an opening CCV and samples are analyzed within the next 12-hour time period, then an additional DFTPP tune is not required and the 12-hour time period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a DFTPP tune, followed by an opening CCV, is required and the next 12-hour time period begins with the DFTPP tune.

9.4.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period, another injection of the CCV

solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standard/spiking solutions and blanks must be allowed to warm to ambient temperature before preparation or analysis.

9.4.3.2 Add sufficient amount of internal standard solution (Section 7.2.3.6) to an aliquot of CCV standard to result in 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.3.6 should permit most of the semivolatile target compounds to have RRTs of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

9.4.3.3 Analyze the CCV standard by injecting 1.0 or 2.0 µL of standard.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each semivolatile target compound and DMC using Equation 1 and the primary characteristic ions found in Table 3. For internal standards, use the primary ions listed in Table 3 unless interferences are present. If interferences prevent the use of the primary ion for a given internal standard, use the secondary ion(s) listed in Table 3.

9.4.4.2 Calculate the Percent Difference (%Difference) between the $\overline{RRF}$ from the most recent initial calibration and the continuing calibration verification RRF for each semivolatile target compound and DMC using Equation 3.

EQ. 3 Relative Response Factor Percent Difference Calculation

$$\%\ \text{Difference}_{RRF} = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_c}} \times 100$$

Where,

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration meeting technical acceptance criteria.

RRF_c = Relative Response Factor from CCV standard.

9.4.5 Technical Acceptance Criteria for Opening and Closing Continuing Calibration Verification (CCV)

9.4.5.1 The opening and closing CCV standard must be analyzed at or near the mid-point concentration level of the calibration standards, normally 20 ng/µL, at the frequency described in Section 9.4.2, on a GC/MS system meeting the instrument performance check and the initial calibration technical acceptance criteria.

NOTE: For the optional analysis of PAHs/pentachlorophenol, the opening and closing CCV standard must be analyzed at or near

the mid-point concentration level of the calibration range for SIM analysis, normally 0.40 ng/µL, at the frequency described in Section 9.4.2, and on a GC/MS system meeting the initial calibration technical acceptance criteria.

9.4.5.2 For an opening CCV, the RRF for each semivolatile target compound and DMC must be greater than or equal to the compound's minimum acceptable RRF listed in Table 4. For a closing CCV, the RRF for each semivolatile target compound and DMC must be greater than or equal to 0.010.

9.4.5.3 For an opening CCV, the RRF Percent Difference for each semivolatile target compound that must be within the inclusive range listed in Table 4. For a closing CCV, the RRF Percent Difference for each semivolatile target compound must be in the inclusive range of ±50.

9.4.5.4 For an opening CCV, up to four semivolatile target compounds may fail to meet the requirements listed in Sections 9.4.5.2 and 9.4.5.3 (excluding those compounds that have a minimum RRF of 0.010 and a maximum Percent Difference), but the RRFs of those four compounds must be greater than or equal to 0.010, and the Percent Differences must be within the inclusive range of ±40%. For a closing CCV, all target compounds must meet the requirements listed in Section 9.4.5.2 and 9.4.5.3 for a closing CCV.

9.4.5.5 For the optional analysis of PAHs/pentachlorophenol using the SIM technique, up to two semivolatile target compounds may fail to meet the criteria listed in Sections 9.4.5.2 and up to two semivolatile target compounds may fail to meet the criteria listed in 9.4.5.3 for the opening CCV. However, the RRFs of those two compounds must be greater than or equal to 0.010, and the Percent Difference must be within the inclusive range of ±40%. All PAH and phenolic compounds must meet the criteria listed in Sections 9.4.5.2 and 9.4.5.3 for a closing CCV.

9.4.5.6 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Opening and Closing CCV

9.4.6.1 If the opening CCV technical acceptance criteria in Sections 9.4.5.2 and 9.4.5.3 are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria in Sections 9.4.5.2 and 9.4.5.3 are not met, then all samples and blanks analyzed within that 12-hour time period must be reanalyzed at no additional cost to USEPA. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.2 CCV technical acceptance criteria MUST be met before any samples or required blanks, are analyzed. Any samples or required blanks analyzed when CCV criteria have not been met will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all of the sample cleanup procedures presented in this Exhibit, including those included by reference. The Contractor may use any of the procedures or combinations of procedures to cleanup the samples prior to analysis, unless the Contractor is specifically directed by the Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including Method Detection Limits (MDLs) (see Section 12.3) and any precision and recovery limits.

NOTE: If Selected Ion Monitoring (SIM) analysis is requested for a sample, a full scan analysis at the regular concentration levels must be performed on that sample prior to the SIM analysis. For all SIM target compounds detected at or above Contract Required Quantitation Limits (CRQLs) during the full scan analysis, a SIM analysis is not to be performed for that target compound. Any SIM analyses not performed for this reason must be noted in the Sample Delivery Group (SDG) Narrative.

10.1 Sample Preparation

10.1.1 If an insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed, or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.2 If multi-phase samples (e.g., a two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample;
- Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases;
- Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside the scope), the Region may require the Contractor to do any of the following:

- Separate the phase(s) and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.

- Do not analyze the sample.

10.1.2.2 No other change in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water Samples

10.1.3.1 Continuous liquid-liquid extraction is used to extract the samples. Separatory funnel extraction or other manual extraction techniques cannot be used. Allow the sample to come to ambient temperature.

10.1.3.2 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.2.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom sidearm.

10.1.3.2.3 Measure out a 1.0 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure and record the initial pH of the sample with a pH meter or narrow range pH paper. Adjust the pH to 2.0 with 1:1 sulfuric acid and record the final pH.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.4 Using a syringe or volumetric pipet, add a sufficient amount of the Deuterated Monitoring Compound (DMC) standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of the SIM DMCs (fluoranthene-d_{10} and 2-methylnapthalene-d_{10})(Section 7.2.3.1) into the sample and mix well.

10.1.3.2.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample was received in a 1 L container, rinse the empty container with 50 mL of methylene chloride and add rinsate to the continuous extractor.

10.1.3.2.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.3 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.3.1 Follow the procedure in Sections 10.1.3.2.1 - 10.1.3.2.6 but reduce the amount of methylene chloride used to 50 mL and extract for a minimum of 6 hours.

10.1.3.3.2 Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to assure efficient extraction of the sample and extend the extraction time by a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used.

10.1.3.3.3 It may not be necessary to dry the extract with sodium sulfate, if the hydrophobic membrane type extractor is used.

10.1.3.4 If low DMC recoveries occur, assure: 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; and 3) there was proper cooling for condensation of solvent.

10.1.3.5 Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instruction for set-up.

10.1.4 Soil/Sediment Samples

Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment to a 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine the pH of the sample with a pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil/sediment is greater than 11 or less than 5, document this in the SDG Narrative. Discard this portion of the sample.

NOTE: If limited sample weight (less than 50 g) is received, use a smaller 1:1 ratio of grams of soil/sediment sample to mLs of water for the pH determination. Note this in the SDG Narrative.

10.1.4.2 Percent Moisture

Immediately after weighing the sample for extraction, weigh 5-10 g of the soil/sediment into a tared crucible. Determine the Percent Moisture (%Moisture) by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual

analytes will be reported relative to the dry weight of soil/sediment.

NOTE: If a soil sample has greater than 65% moisture, the laboratory may use up to 50 g of soil sample in order to achieve the expected CRQLs. The amount of sample used and the Percent Moisture should be noted in the SDG Narrative.

EQ. 4 Percent Moisture Calculation

$$\%\ \text{Moisture} = \frac{\text{grams of wet sample - grams of dry sample}}{\text{grams of wet sample}} \times 100$$

10.1.4.3 Mandatory Determination of Concentration Level

The Contractor must determine whether a soil/sediment sample should be analyzed by the low-level or medium-level soil/sediment method. It is the responsibility of the Contractor to analyze the sample at the correct level.

- Assume the sample is low-level and analyze a 30 g sample. An analysis using the wrong level because of incorrect assumption will not be billable to USEPA.
- Use USEPA screening procedures or an in-house laboratory screening procedure. The procedure must be documented and available for review during on-site laboratory evaluation, or when requested by the USEPA Regional Contract Laboratory Program Project Officer (CLP PO).

10.1.4.4 Low-Level Soil/Sediment Samples

10.1.4.4.1 Three procedures are provided for the extraction of semivolatile compounds from soil/sediment samples:

- Ultrasonic extraction;
- [Automated] Soxhlet extraction; and
- Pressurized fluid extraction.

The Contractor shall use one of the above procedures for the extraction of soil/sediment samples.

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.4.2 For soil/sediment sample extractions, perform the following steps rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g, into a 400 mL beaker. Add 60 g of anhydrous powdered or granulated sodium sulfate, or 30 g of Hydromatrix, and mix well to produce a sandy texture. Proceed to Section 10.1.4.4.3 for ultrasonic extraction, Section 10.1.4.4.4 for automated Soxhlet extraction, or Section 10.1.4.4.5 for pressurized fluid extraction.

NOTE: For samples extracted by the Pressurized Fluid Extraction procedure (Section 10.1.4.3.5) the use of sodium sulfate is not recommended.

10.1.4.4.3 Ultrasonic Extraction

10.1.4.4.3.1 Add a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of the SIM DMCs (fluoranthene-d_{10} and 2-methylnapthalene-d_{10})(Section 7.2.3.1) to the sample, then immediately add 100 mL of 1:1 v/v methylene chloride/acetone.

10.1.4.4.3.2 Place the bottom of the tip of the 3/4 inch tapered disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do not use a microtip probe.

10.1.4.4.3.3 Sonicate for 3 minutes using a 3/4 inch disrupter horn at full power, (output control knob at 10) with pulse on and percent duty cycle knob set at 50%.

Decant and filter extracts through Whatman No. 41 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.4.4.3.4 Repeat the extraction two more times with two additional 100 mL portions of 1:1 v/v methylene chloride/acetone. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the unenergized probe. Decant the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 v/v methylene chloride/acetone.

10.1.4.4.3.5 If the sample is to be screened following the low-level preparation method prior to Gel Permeation Chromatography (GPC), proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.4.4.4 [Automated] Soxhlet Extraction

10.1.4.4.4.1 The Contractor may use either automated or non-automated Soxhlet extraction. Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minute to prevent solvent loss through the condensers.

10.1.4.4.4.2 Transfer the entire sample from the beaker (Section 10.1.4.4.2) to the thimble. Add a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of each SIM DMC (fluoranthene-d_{10} and 2-methylnapthalene-d_{10}) (Section 7.2.3.1) to the sample.

10.1.4.4.4.3 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.4.4.4.4 Insert the extraction cups containing boiling chips, and load each with appropriate volume of extraction solvent (1:1 v/v methylene chloride/acetone). Using the cup holder, lower the

locking handle, ensuring that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.4.4.4.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 min. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.4.4.4.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set the timer for 60 min. Condenser valves are still open. Extract for the preset time. After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.4.4.4.7 When all but 2-5 mL of the solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with methylene chloride and add the rinsates to the glass tubes.

10.1.4.4.4.8 If the sample is to be screened following the low-level preparation method prior to GPC, proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.4.4.5 Pressurized Fluid Extraction

10.1.4.4.5.1 Transfer the entire sample from the beaker (Section 10.1.4.4.2) to an extraction cell of the appropriate size for the aliquot. Add sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg for each SIM DMC (fluoranthene-d_{10} and 2-methylnapthalene-d_{10} (Section 7.2.3.1) to the sample.

10.1.4.4.5.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.4.4.5.3 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.4.4.5.4 The following are recommended extraction conditions.

Extraction Conditions	
Oven temperature	100°C
Pressure	1500-2000 psi
Static time	5 min. (after 5 min. pre-heat equilibration)
Flush volume	60% of the cell volume
Nitrogen purge	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles	1

10.1.4.4.5.5 Optimize the extraction conditions as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.4.4.5.4.

10.1.4.4.5.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.4.4.5.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete.

10.1.4.4.5.8 If the sample is to be screened following the low-level preparation method prior to GPC, proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.4.5 Medium-Level Soil/Sediment Samples

10.1.4.5.1 The procedure described below is for the extraction of soil/sediment samples by the ultrasonic method (Section 10.1.4.4.3). The Contractor may also use the [automated] Soxhlet extraction or pressurized fluid extraction procedures described in Sections 10.1.4.4.4 and 10.1.4.4.5, respectively. The requirements of this analytical method must be met at all times [i.e., sample weight used for medium-level soil/sediment extraction and original CRQLs for medium-level soils]. As applicable, follow the manufacturer's instructions for the use of all extraction equipment.

NOTE: All medium-level soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.5.2 Transfer approximately 1 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

10.1.4.5.3 Add 2.0 g or sufficient quantity of anhydrous powdered or granulated sodium sulfate or Hydromatrix to the sample in the 20 mL vial and mix well to produce a sandy texture.

10.1.4.5.4 DMCs are added to all samples, Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and blanks. Add a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC excluding the two SIM DMCs (fluoranthene-d_{10} and 2-methylnapthylene-d_{10}) (Section 7.2.3.1) to the sample mixture.

10.1.4.5.5 Immediately add sufficient methylene chloride to the sample so that the total volume is approximately 10 mL and disrupt the sample with the 1/8 inch tapered microtip ultrasonic probe for 2 minutes at output control setting 5, in continuous mode. Before extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. Decant and filter extract through Whatman No. 41 (or equivalent) filter paper

using vacuum filtration or centrifuge and decant extraction solvent.

NOTE: Concentration of the extracts of soil/sediment samples prepared by the medium-level procedure described above may not be necessary. Proceed to Section 10.2.1.6 if no extract concentration is to be performed.

10.2 Concentrating the Extract

Note that low-level soil/sediment samples prepared by the procedure described in Section 10.1.4.4 will result in extracts containing a mixture of acetone and methylene chloride. Because all soil/sediment sample extracts MUST be subjected to GPC cleanup prior to analysis, the majority of the acetone must be removed from the extract, otherwise, it will have adverse effects on the GPC column. To remove the acetone from the soil/sediment sample extract, follow the steps in Section 10.2.1, then concentrate to 1.0 mL using the nitrogen evaporation technique in Section 10.2.2.2.

10.2.1 Concentration by Kuderna-Danish (K-D)

10.2.1.1 Assemble a K-D apparatus by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all the semivolatile target compounds listed in Exhibit C (Semivolatiles).

10.2.1.2 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.2.1.2.1 For soil/sediment samples, directly transfer the extract to the K-D concentrator.

10.2.1.2.2 Rinse the Erlenmeyer flasks (for both water and soil/sediment samples) and the column (for water samples) with 20-30 mL of methylene chloride to complete the quantitative transfer.

10.2.1.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-15 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 or 2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

10.2.1.4 For water samples that do not require GPC cleanup, proceed to final concentration of extract (Section 10.2.2). Oily water samples require GPC.

10.2.1.5 For water samples that require GPC, adjust the volume of the extract to 10.0 mL with methylene chloride and proceed with GPC cleanup (Section 10.3).

10.2.1.6 For soil/sediment samples, adjust the volume of the extract to 10.0 mL with methylene chloride and proceed with GPC cleanup (Section 10.3).

10.2.1.7 For water samples or soil/sediment samples that have undergone GPC, proceed to final concentration of extract (Section 10.2.2).

10.2.2 Final Concentration of Extract

Two different concentration techniques are permitted to obtain the final extract volume, Micro Snyder Column and Nitrogen Evaporation techniques:

10.2.2.1 Micro Snyder Column Technique

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL (0.4 mL for low-level soil/sediment samples or water samples that have undergone GPC), remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the evaporative flask and its lower joint into the concentrator tube with 0.2 mL (O.1 mL for low-level soil/sediment samples and water samples that have undergone GPC) of methylene chloride. Adjust the final volume to 1.0 mL (0.5 mL for low-level soil/sediment samples and water samples that have undergone GPC) with methylene chloride. Transfer the extract to the polytetrafluoroethylene (PTFE)-sealed screw-cap bottle, label the bottle, and store at 4°C (±2°C).

10.2.2.2 Nitrogen Evaporation Technique (Taken from ASTM Method D3086)

The following method may be used for final concentration of the semivolatile extract instead of the procedure in Section 10.2.2.1. Place the concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to just below 1 mL (below 0.5 mL for low-level soil/sediment samples and water samples that have undergone GPC) by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) above the extract.

CAUTION: Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or PTFE tubing. New plastic tubing must not be used between the carbon trap and the sample since it may introduce interferences.

The internal wall of the concentrator tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the

water level of the bath. The extract must never be allowed to become dry.

10.2.2.3 Final Extract Volumes

The final extract volumes in Sections 10.2.2.3.1 and 10.2.2.3.2 are recommended volumes. If more sensitive Gas Chromatograph/Mass Spectrometer (GC/MS) systems are employed, then the larger extract volumes (less concentrated extracts) may be used, provided that the CRQLs for all target compounds can be achieved, and that all DMCs and internal standards have an expected extract concentration that is at the mid-point of the calibration curve.

10.2.2.3.1 Water

For water samples that did not undergo GPC, the extract must be brought to a final volume of 1.0 mL with methylene chloride. Remove boiling chips before adjusting final volume. For water samples that underwent GPC, the extract must be brought to a final volume equal to V_{out} (volume of extract collected from GPC cleanup) with methylene chloride [concentrating the extract to 0.5 mL will result in no loss of sensitivity despite the volume of extract (5 mL) not recovered after GPC].

10.2.2.3.2 Soil/Sediment

Adjust the final volume for low-level and medium-level soil/sediment samples to equal V_{out} with methylene chloride. For example, if V_{out} equals 0.5 mL, then the final volume must be adjusted to 0.5 mL. Concentrating the extract to 0.5 mL will result in no loss of sensitivity despite the volume of extract not recovered after GPC cleanup. Remove boiling chips before adjusting final volume.

10.2.2.3.3 Transfer the extract to a PTFE-sealed screw-cap bottle, label the bottle, and store at 4°C (±2°C).

10.3 Sample Cleanup by Gel Permeation Chromatography (GPC)

10.3.1 Introduction

10.3.1.1 GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.3.1.2 GPC must be performed for all soil/sediment extracts. GPC must be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. In addition, GPC must be performed for all associated blanks, and MS/MSDs. If the cleanup procedure is inadequate, contact SMO.

10.3.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternative column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC Continuing Calibration Verification (CCV), and 2) the column packings do not introduce

contaminants/artifacts into the sample that interfere with the analysis of the semivolatile compounds. Follow the manufacturer's instructions for preparation of the GPC column.

10.3.3 Calibration of GPC

10.3.3.1 Summary of GPC Calibration and GPC Continuing Calibration Verification

The GPC calibration procedure and GPC CCV procedure are based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.3.3.2 Frequency of GPC Calibration and GPC Continuing Calibration Verification

Each GPC system must be calibrated upon award of a contract, when the column is changed, when channeling occurs, and once every 7 days [GPC CCV] when samples, including MS/MSDs and blanks, are cleaned up using GPC.

10.3.3.3 Procedure for GPC Calibration and GPC Continuing Calibration Verification

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte Retention Times (RTs) and must be monitored.

10.3.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.3.3) onto the GPC. Establish appropriate "COLLECT" and "DUMP" time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of bis (2-ethylhexyl) phthalate and after the elution of corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "WASH" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences.

10.3.3.3.2 Re-inject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.3.3.3.3 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

10.3.3.3.4 Analyze a GPC blank of methylene chloride after each GPC calibration or each GPC CCV. Concentrate the methylene chloride that passes through the system during the collect cycle using a K-D evaporator. Add internal standards at the appropriate concentration and analyze the concentrate by Gas Chromatograph/Mass Spectrometer (GC/MS).

10.3.4 Technical Acceptance Criteria for GPC Calibration and GPC Continuing Calibration Verification

10.3.4.1 The GPC system must be calibrated and verified at the frequency described in Section 10.3.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and the phthalate peaks should exhibit greater than 85% resolution.
- The phthalate and methoxychlor peaks should exhibit greater than 85% resolution.
- Methoxychlor and perylene peaks should exhibit greater than 85% resolution.
- Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.

10.3.4.2 The solvent flow rate and column pressure must be within the manufacturer's specified ranges.

10.3.4.3 If the RT shift is greater than 5% between calibrations take corrective action. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.4.4 A copy of the two most recent ultraviolet (UV) traces of the calibration solution from the same GPC system (instrument, column, conditions) must be submitted with the data for the associated samples.

10.3.4.5 The analyte concentrations in the GPC blank must be less than the CRQL for all target compounds in Exhibit C (Semivolatiles), except bis(2-ethylhexyl)phthalate, which must be less than 5 times the CRQL.

10.3.5 Corrective Action for GPC Calibration and GPC Continuing Calibration Verification

10.3.5.1 If the requirements in Section 10.3.4 cannot be met, the column may be cleaned by processing several 5 mL volumes of butylchloride through the system. Butylchloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore the performance of the column, the column must be repacked with new packing and recalibrated. It may be necessary to obtain a new lot of Bio Beads if the column fails all criteria.

10.3.5.2 If the GPC blank exceeds the requirements in Section 10.3.4.5, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.4 Sample Extract Cleanup by GPC

10.4.1 It is very important to have constant laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not constant, RTs will shift, and the "DUMP" and "COLLECT" times determined by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C.

10.4.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 40 mg/mL of non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or other suitable container. Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is being injected on the column. Viscous extracts or extracts containing a large amount of non-volatile residue will cause problems with an automated injection system's ability to inject the proper amount of sample extract on a column. After the sample extract has been processed, the remaining sample extract in the injection vial must be checked before proceeding with extract cleanup to assure that the proper amount was injected on the column. If the proper amount of extract was not injected, the sample must be re-prepared at no additional cost to USEPA, and the sample extract must either be diluted and loaded into several loops, or the sample extract must be injected manually.

NOTE: When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected from each run.

10.4.3 Frequency of GPC Sample Cleanup

GPC cleanup must be performed once for each soil/sediment extract and for water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes. GPC cleanup on the method blank must be performed after all associated samples have been cleaned up (GPC sequence: calibration, sample 1, sample 2, etc., method blank, calibration verification).

10.4.4 Procedure for GPC Sample Cleanup

10.4.4.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap). Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

NOTE: Some GPC instrument manufacturers recommend using a smaller micron size filter. Follow the manufacturer's recommended operating instructions.

10.4.4.2 Introduction of particulates or glass wool into the GPC switching valves may require factory repair of the apparatus.

10.4.4.3 Follow the manufacturer's instructions for operation of the GPC system being utilized. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL injection loop is used, concentrate the sample extract to 4 mL instead of 10 mL and inject 2 mL instead of 5 mL.

10.4.4.4 If the sample is difficult to load, part of the system may be blocked. Take appropriate corrective action, following the manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

10.4.4.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.4.4.6 After loading all the sample loops, process each sample using the "COLLECT" and "DUMP" cycle time established in Section 10.3.3.3.1.

10.4.4.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems.

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure.
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.
- Leaks in the system or significant variances in room temperature.

10.4.4.8 Any samples that were loaded into two or more loops must be recombined before proceeding with concentration.

10.5 Final Concentration

Concentrate the extract as per Section 10.2.2. After removing boiling chips, final volumes should be brought to the volumes stated in Section 10.2.2.3.

10.6 Sample Analysis by Gas Chromatograph/Mass Spectrometer (GC/MS)

10.6.1 Sample extracts shall be analyzed only after the GC/MS system has met the instrument performance check, initial calibration, and CCV requirements. The same instrument conditions must be employed for the analysis of samples as were used for calibration.

10.6.2 The internal standard solution is added to an aliquot of each sample extract. Add sufficient amount of the internal standard solution (Section 7.2.3.6) to each accurately measured aliquot of water, low-

level, or medium-level soil/sediment sample extract to result in 20 ng/µL concentration of each internal standard.

NOTE: In order to make provision for sample dilutions and/or optional analysis of Polyaromatic Hydrocarbons (PAHs)/pentachlorophenol by the Selected Ion Monitoring (SIM) technique, if requested, the internal standard solution must be added to aliquots of sample extracts, not the entire extract.

10.6.3 If the optional analysis of PAHs/pentachlorophenol by SIM is to be performed, the Contractor shall add sufficient amount of the internal standard solution to each accurately measured aliquot of water and low- level soil/sediment sample extract to result in a 0.40 ng/µL concentration of each internal standard.

10.6.4 If sample extracts are to be diluted, add internal standards after dilution. Internal standards must be added to maintain the required 20 ng/µL (0.40 ng/µL for the optional analysis of PAHs/pentachlorophenol by SIM) of each internal standard in the extract volume.

10.6.5 Inject 1.0 or 2.0 µL of the sample extract into the GC/MS. This volume must contain each internal standard at a concentration of 20 ng/µL (0.40 ng/µL for optional analysis of PAHs/pentachlorophenol by SIM).

10.6.6 Sample Dilutions

10.6.6.1 If the response of any target compound in any sample exceeds the response of the same target compound in the high standard of the initial calibration, that sample extract must be diluted. Add the internal standard solution to the diluted extract for a concentration of 20 ng/µL (0.40 ng/µL for optional analysis of PAHs/pentachlorophenol by SIM) of each internal standard, and analyze the diluted extract. Guidance in performing dilution and exceptions to this requirement are given below.

10.6.6.2 Use the results of the original analysis to determine the approximate Dilution Factor (DF) required to get the largest analyte peak within the initial calibration range.

10.6.6.3 The DF chosen must keep the response of the largest peak for a target compound in the upper half of the calibration range of the instrument.

10.6.6.4 The maximum DF permitted for low-level soils is 30.0. If a low-level soil sample requires a DF greater than 30.0 to bring target compounds within the calibration range, then the medium-level method shall be utilized.

10.6.6.5 If more than two analyses (i.e., from the original sample extract and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO for guidance.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL) in Exhibit C (Semivolatiles), shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample analyte within the Gas Chromatograph (GC) Relative Retention Time (RRT) unit window established from the 12-hour calibration standard.
- Correspondence of the sample analyte and calibration standard component mass spectra.

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the analyte Retention Times (RTs) to those from the 20 ng/µL [0.40 ng/µL for the optional Polyaromatic Hydrocarbons (PAHs)/pentachlorophenol analysis] calibration standard. Otherwise, use the corresponding opening Continuing Calibration Verification standard. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using Extracted Ion Current Profiles (EICPs) for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained from a calibration standard on the Contractor's Gas Chromatograph/Mass Spectrometer (GC/MS) meeting the daily instrument performance requirements for decafluorotriphenylphosphine (DFTPP) are required. Once obtained, these standard spectra may be used for identification purposes only if the Contractor's GC/MS meets the DFTPP daily instrument performance requirements.

11.1.1.4 The requirement for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- The relative intensities of ions specified in the paragraph above must agree within ±20% between the standard and sample spectra (e.g., For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).
- Ions greater than 10% in the sample spectrum, but not present in the standard spectrum, must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their

spectra. When target compounds are below Contract Required Quantitation Limits (CRQLs) but the spectrum meets the identification criteria, report the concentration with a "J". For example, if the CRQL is 5.0 µg/L and concentration of 3.0 µg/L is calculated, report as "3.0J".

11.1.1.5 If a compound cannot be verified by all of the spectral identification criteria in Sections 11.1.1.1 - 11.1.1.4, but in the technical judgement of the mass spectra interpretation specialist the identification is correct, then the Contractor shall report the identification and proceed with quantitation.

11.1.2 Qualitative Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library, shall be used as the reference library.

11.1.2.2 All organic compounds that have not been positively identified as semivolatile target analytes using the procedures detailed in Section 11.1.1, or that are not Deuterated Monitoring Compounds (DMCs) or internal standards shall be tentatively identified via a forward search of the NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form I SV-TIC. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes" on Form I SV-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} that contains only C-H and C-C single bonds. The concentrations of each of the alkanes is to be summed and reported as a single result for the "total alkanes". Documentation for the tentative identification of each alkane shall be supplied in the hard copy deliverable packages. The alkanes are not to be counted as part of the 30 compounds individually reported as TICs on Form I SV-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be quantified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Peaks that are suspected to be a aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched, reported, and counted as part of the 30 most intense non-target semivolatile compounds, and qualified with an "A" flag on Form I SV-TIC.

11.1.2.5 Rules for Making Tentative Identification

11.1.2.5.1 For compounds to be reported, as per the instructions in Section 11.1.2.3., identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The

compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.1.2.5.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the semivolatile target analyte list, unless the library search produces only one compound having a match of greater than 85%, and that compound is identified as a DMC, internal standard, or semivolatile target analyte.

11.1.2.5.3 If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.5.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a TIC has obvious isomer analogs, the laboratory shall include in the SDG narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.5.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialist is encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.1.2.6 Qualitative identification on non-target compounds is not required when performing SIM analyses.

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Target compounds identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table 2). The EICP area of primary characteristic ions of analytes listed in Table 3 are used for quantitation.

11.2.1.2 It is expected that situations will arise when the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In

these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific TCL compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet Quality Control (QC) criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instance of manual integration must be documented in the SDG Narrative.

11.2.1.3 In all instances where the data system report has been edited or where manual integration or quantitation has been performed, the GC/MS Operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Semivolatiles), internal standards, and DMCs.

11.2.1.4 The requirements listed in Sections 11.2.1.1 - 11.2.1.3 apply to all standards, samples, and blanks.

11.2.1.5 The Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration is used to calculate the concentration in the sample. Secondary ion quantitation is allowed ONLY when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reason in the SDG Narrative. The area of a secondary ion cannot be used for the area of a primary ion unless a $\overline{RRF}$ is calculated using the secondary ion.

11.2.1.6 Calculate the concentration in the sample using the $\overline{RRF}$ and Equations 5 and 6.

11.2.1.6.1 Water

EQ. 5 Concentration of Water Sample

$$\text{Concentration } \mu g/L = \frac{(A_x)\,(I_s)\,(V_t)\,(DF)\,(GPC)}{(A_{is})\,(\overline{RRF})\,(V_o)\,(V_i)}$$

Where,

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard injected in ng.

V_o = Volume of water extracted in mL.

V_i = Volume of extract injected in µL.

V_t = Volume of the concentrated extract in µL (If GPC Cleanup is performed, $V_t = V_{out}$).

$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard.

$GPC = \frac{V_{in}}{V_{out}}$ = GPC factor. (If no GPC is performed, GPC = 1).

V_{in} = Volume of extract loaded onto GPC column.

V_{out} = Volume of extract collected after GPC cleanup.

DF = Dilution Factor. The DF for analysis of water samples for semivolatiles by this method is defined as follows:

$$DF = \frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

11.2.1.6.2 Soil/Sediment

EQ. 6 Concentration of Soil/Sediment Sample

$$\text{Concentration µg/Kg (Dry weight basis)} = \frac{(A_x)\,(I_s)\,(V_t)\,(DF)\,(GPC)}{(A_{is})\,(\overline{RRF})\,(V_i)\,(W_s)\,(D)}$$

Where,

A_x, I_s, A_{is}, V_{in}, and V_{out} are as given for water, above.

V_t = Volume of the concentrated extract in µL (If no GPC Cleanup is performed, then V_t = 1000 µL. If GPC Cleanup is performed, then $V_t = V_{out}$).

V_i = Volume of the extract injected in µL.

$$D = \frac{100 - \%\ \text{Moisture}}{100}$$

W_s = Weight of sample extracted in g.

$GPC = \frac{V_{in}}{V_{out}}$ = GPC Factor

$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard.

DF = Dilution Factor. The DF for analysis of soil/sediment samples for semivolatiles by this method is defined as follows:

$$DF = \frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

A GPC factor of 2.0 is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup. Concentrating the extract collected after GPC to 0.5 mL maintains the sensitivity of the soil/sediment method.

11.2.2 Non-Target Compound

An estimated concentration for non-target compounds tentatively identified shall be quantitated by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used. The equations for calculating concentration are the same as Equations 5 and 6. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compounds to be measured and the internal standard. An $\overline{RRF}$ of 1 is to be assumed. The resulting concentration shall be qualified as "J" (estimated, due to lack of a compound specific response factor), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. An estimated concentration should be calculated for all TICs as well as those identified as unknowns.

11.2.3 CRQL Calculations

11.2.3.1 Water Samples

EQ. 7 Aqueous Adjusted CRQL

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(V_x)\,(V_t)\,(DF)}{(V_o)\,(V_c)}$$

Where,

V_t, DF, and V_o are as given in Equation 5.

V_x = Contract sample volume (1000 mL).

V_c = Contract concentrated extract volume (1000 µL if GPC is not performed. If GPC was performed, then $V_c = V_{out}$).

11.2.3.2 Soil/Sediment Samples

EQ. 8 Soil/Sediment Adjusted CRQL

$$\underset{\text{CRQL}}{\text{Adjusted}} = \underset{\text{CRQL}}{\text{Contract}} \times \frac{(W_x)\,(V_t)\,(DF)}{(W_s)\,(V_c)\,(D)}$$

Where,

V_t and DF = As given in Equation 5.

W_s and D = As given in Equation 6.

W_x = Contract sample weight (30 g for low-level soil/sediment samples and 1.0 g for medium-level soil/sediment samples).

V_c = Contract concentrated extract volume (If GPC is required, $V_c = V_{out}$).

11.2.4 Deuterated Monitoring Compound (DMC) Recoveries

11.2.4.1 Calculate DMC recoveries for all samples, blanks, and Matrix Spike and Matrix Spike Duplicates (MS/MSDs). Determine if recovery is within limits (Table 6) and report on the appropriate form.

11.2.4.2 Calculate the concentrations of the DMCs using the same equations as used for the target compounds. Calculate the recovery of each DMC using the following equation:

EQ. 9 DMC Percent Recovery Calculation

$$\%\ \text{Recovery} = \frac{(\text{Concentration (or amount) found} \times DF)}{\text{Concentration (or amount) spiked}} \times 100$$

Where,

DF = Same as EQ. 5.

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The samples must be analyzed on a GC/MS system meeting the instrument performance check, initial calibration, CCV, and blank technical acceptance criteria. The sample must undergo cleanup procedures, when required, on a GPC meeting the technical acceptance criteria for GPC calibration.

11.3.2 The sample must be extracted and analyzed within the contract holding times.

11.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.3.4 The Percent Recoveries of DMCs in a sample must be within the recovery limits listed in Table 6. Up to four DMCs per sample may fail to meet the recovery limits listed in Table 6 but all Percent

Recoveries must be greater than zero. If the optional analysis of PAHs and pentachlorophenol using the Selected Ion Monitoring (SIM) technique is to be performed, both SIM DMCs must meet the recovery limits in Table 6.

NOTE: The DMC recovery requirements do not apply to samples that have been diluted.

11.3.5 The instrumental response (EICP area) for each of the internal standards in the sample must be within the range of 50.0% and 200% of the response of the internal standard in the most recent opening CCV standard analysis.

11.3.6 The RT shift for each of the internal standards must be within ±0.50 min. (30 seconds) between the sample and the most recent opening CCV standard analysis.

11.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample extract is also analyzed according to the procedures in Section 10.6.6.

11.4 Corrective Action for Sample Analysis

11.4.1 Corrective Action for Sample Analysis

The sample technical acceptance criteria **must** be met before data are reported. Samples contaminated from laboratory sources, or sample results submitted not meeting the sample technical acceptance criteria, will require reextraction and/or reanalysis at no additional cost to USEPA.

11.4.2 Corrective action for failure to meet instrument performance checks and initial and continuing calibration verification must be completed before the analysis of samples.

11.4.3 Corrective Action for DMC Recoveries that Fail to Meet Their Acceptance Criteria (Section 11.3.4, Table 6)

11.4.3.1 If the DMC recoveries in a sample fail to meet the acceptance criteria specified in Section 11.3.4, check calculations, sample preparation logs, DMC standard spiking solutions, and the instrument operation.

- If the calculations were incorrect, correct them and verify that the DMC recoveries meet their acceptance criteria.
- If the sample preparation logs indicate that the incorrect amount of DMC standard spiking solution was added to the sample, then reextract and reanalyze the sample after adding the correct amount of DMC standard spiking solution.
- If the DMC standard spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solution, and reextract and reanalyze the sample.
- If the DMC recoveries were outside the lower acceptance limit and the extract from the sample were cleaned up on a GPC using an automated injection system, the Contractor shall verify that the proper amount was injected on the GPC column.

If insufficient sample volume was injected on the GPC, the sample must be re-prepared and reanalyzed.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the DMC recoveries meet their acceptance criteria.

- If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the sample extract.

11.4.3.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

11.4.3.2.1 Reextract and reanalyze the sample. EXCEPTION: If DMC recoveries in a sample used for an MS/MSD were considered unacceptable, then it should be reextracted/reanalyzed only if DMC recoveries met the acceptance criteria in <u>both</u> the MS/MSD analyses.

11.4.3.2.2 If the DMC recoveries meet acceptance criteria in the reextracted/reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit only data from the reextraction/reanalysis.

11.4.3.2.3 If the DMC recoveries fail to meet the acceptance criteria in the reextracted/reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the reextraction/reanalysis on all deliverables, using the suffixes in Exhibit B, Section 3.3.7.1.

11.4.4 Corrective Action for Internal Standard Compound Responses that Fail to Meet Their Acceptance Criteria (Sections 11.3.6 and 11.3.7)

11.4.4.1 If the internal standards in a sample fail to meet their acceptance criteria, check calculations, internal standard solutions, and instrument operation.

- If the calculations were incorrect, correct them, and verify that the internal standard responses meet their acceptance criteria.

- If the internal standard solution was improperly prepared, concentrated, or degraded, re-prepare solutions and reanalyze another aliquot of the sample extract after adding the correct amount of the freshly prepared internal standard solution.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract.

- If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

11.4.4.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

11.4.4.2.1 Reanalyze the sample extract. EXCEPTION: If internal standard compound recoveries in a sample used for a Matrix Spike and/or

Matrix Spike Duplicate were outside the acceptance windows, then it should be reanalyzed only if internal standard compound recoveries met the internal standard acceptance criteria in both the MS/MSD analysis.

11.4.4.2.2 If the internal standard compound recoveries meet acceptance criteria in the reanalyzed sample extract, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis.

11.4.4.2.3 If the internal standard compound recoveries fail to meet their acceptance windows in the reanalyzed sample extract, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B.

11.4.5 Corrective Action for Internal Standard Compound RTs Outside Acceptance Criteria (Section 11.3.7)

11.4.5.1 If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

11.4.5.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

11.4.5.2.1 Reanalyze the sample extract.

EXCEPTION: If the internal standard compound RTs in a sample used for a Matrix Spike and/or Matrix Spike Duplicate were outside the acceptance criteria, then it should be reanalyzed only if the internal standard compound RTs were within the acceptance criteria in <u>both</u> of the MS/MSD analyses.

11.4.5.2.2 If the internal standard compound RTs are within the acceptance criteria in the reanalyzed sample extract, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis with the internal standard compound RTs within the acceptance limits.

11.4.5.2.3 If the internal standard compound RTs are outside the acceptance criteria in the reanalyzed sample extract, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B, Section 3.3.7.1.

12.0 QUALITY CONTROL (QC)

12.1 Method Blanks

12.1.1 Summary of Method Blanks

A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate or Hydromatrix for soil/sediment samples) spiked with sufficient amount of internal standard solution (Section 7.2.3.6) and Deuterated Monitoring Compound (DMC) standard spiking solution (Section 7.2.3.1) and carried through the entire analytical procedure. The internal standard solution is added just prior to full scan analysis by Gas Chromatograph/Mass Spectrometer (GC/MS). The volume or weight of the reference matrix must be approximately equal to the volume of weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2 Frequency of Method Blanks

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike and Matrix Spike Duplicates (MS/MSDs) and Performance Evaluation (PE) samples]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples; and
- Be analyzed on each GC/MS system used to analyze associated samples and conditions (i.e., GC/MS settings).

12.1.3 Procedure for Method Blank Preparation

12.1.3.1 For semivolatile analyses, a method blank for water samples consists of 1.0 L volume of reagent water spiked with a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of each Selected Ion Monitoring (SIM) DMC (Section 7.2.3.1). For low-level and medium-level soil/sediment samples, a method blank consists of 1 g (medium-level) and 30 g (low-level) of sodium sulfate or Hydromatrix spiked with sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg (low-level) of each SIM DMC. Extract, concentrate, cleanup, and analyze the blank according to procedures for water and soil samples.

12.1.3.2 Under no circumstances should method blanks be analyzed at a dilution (i.e., method blanks should always have a DF = 1.0).

12.1.4 Technical Acceptance Criteria for Method Blank Analysis

12.1.4.1 All blanks must be extracted and analyzed at the frequency described in Section 12.1.2 on a GC/MS system meeting the decafluorotriphenylphosphine (DFTPP), initial calibration, and CCV technical acceptance criteria.

12.1.4.2 The Percent Recovery (%Recovery) of each of the DMCs in the blank must be within the acceptance limits listed in Table 6. These limits are <u>not</u> advisory.

12.1.4.3 The blank must meet the sample acceptance criteria listed in Sections 11.3.5 through 11.3.7.

12.1.4.4 A method blank for semivolatile analysis for low-level soil and water samples must contain less than five times the CRQL of the bis (2-ethylhexyl) phthalate listed in Exhibit C (Semivolatiles). For all other target compounds the method blank must contain less than the Contract Required Quantitation Limit (CRQL) of any single target compound [Exhibit C (Semivolatiles)]. For medium-level soils, the method blank must contain less than the CRQL of any single target compound.

12.1.4.5 All method blanks must be analyzed at the original concentration only (i.e., DF = 1.0).

12.1.5 Corrective Action for Method Blanks

12.1.5.1 If a method blank does not meet the technical acceptance criteria for method blank analysis, the Contractor shall consider the analytical system to be out-of-control.

12.1.5.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvent, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in the GC/MS be eliminated. Samples associated with the contaminated blank must be reextracted and reanalyzed at no additional cost to USEPA.

12.1.5.3 If DMC recoveries in the method blank do not meet the acceptance criteria listed in Section 12.1.4.2 and Table 6, first reanalyze the method blank. If the DMC recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank must be reextracted and reanalyzed at no additional cost to USEPA.

12.1.5.4 If the method blank does not meet internal standard response requirements listed in Section 11.3.6, follow the corrective action procedure outlined in Section 11.4.4.1. The Contractor shall resolve and document the resolution of the problem before proceeding with sample analysis.

12.1.5.5 If the method blank does not meet the Retention Time (RT) requirements for internal standards (Section 11.3.7), check the instrument for malfunction and recalibrate. Reanalyze the method blank. Sample analyses cannot proceed until the method blank meets these requirements.

12.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for semivolatile analyses, USEPA has prescribed a mixture of semivolatile target compounds to be spiked into two aliquots of a sample and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD Analyses

12.2.2.1 An MS/MSD shall be analyzed if requested by the Region [through the Sample Management Office (SMO)] or specified on the Traffic Report/Chain of Custody Record (TR/COC). If requested, a Matrix Spike and a Matrix Spike Duplicate must be performed for each group of 20 field samples in a Sample Delivery Group (SDG), or each SDG, whichever is most frequent. An MS/MSD should be analyzed for each sample matrix (water/soil) and each level (low/med).

12.2.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to the laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 If the USEPA Region requesting MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the Contractor shall choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.

12.2.2.4 If there is insufficient sample remaining in any of the samples in an SDG to perform the requested MS/MSD, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, then the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD analysis performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.2.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis if the Region did not designate samples to be used for this purpose. If the PE sample is an ampulated standard, the ampulated PE sample is not considered to be another matrix type.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water Samples

For water samples, prepare two additional 1.0 L aliquots of the sample chosen for spiking in two continuous extractors. Add a sufficient amount of the DMC standard spiking solution and the matrix spiking solution to each aliquot to result in the addition of 40 µg of each DMC (0.40 µg of each SIM DMC) and 40 µg of each Matrix Spike compound (0.40 µg of each Matrix Spike compound for SIM analysis). Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for water samples (Section 10.1.3).

12.2.3.2 Soil/Sediment Samples - Low-Level

For low-level soil/sediment samples, prepare two additional 30 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in the two 400 mL beakers. Add 60 g of anhydrous powdered sodium sulfate or 30 g of Hydromatrix to each aliquot. Mix well. Add a sufficient amount of the DMC standard spiking solution and the matrix spiking solution to each aliquot, to result in the addition of 40 µg of each DMC (0.40 µg of each SIM DMC) and 40 µg of each Matrix Spike compound (0.40 µg of each Matrix Spike compound for SIM analysis), then follow the appropriate extraction procedure in Section 10.1.4.4. Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for low-level soil samples.

12.2.3.3 Soil/Sediment Samples - Medium-Level

For medium-level soil/sediment samples, prepare two additional 1.0 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in two, 20 mL vials. Add 2.0 g of anhydrous powdered sodium sulfate or 1.0 g of Hydromatrix to each aliquot. Mix well. Add a sufficient amount of DMC standard spiking solution and the matrix spiking solution to result in the addition of 40 µg of each DMC and 40 µg of each Matrix Spike compound, and proceed with the appropriate extraction procedure (Section 10.1.4.5). Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for medium-level samples.

12.2.3.4 For the optional analysis by the SIM method, MS/MSD will not be required unless specifically requested by the Region. If MS/MSD are requested for the optional SIM method, 0.40 µg of only acenaphthene, pentachlorophenol, and pyrene Matrix Spike compounds is required; however, a Matrix Spike solution containing the full list (Section 7.2.4.2.1) at 0.40 µg of each Matrix Spike compound may be used.

12.2.4 Dilution of MS/MSD

Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do <u>not</u> further dilute the MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

Dilution of the sample must be performed in accordance to the conditions in Section 10.6.6.

12.2.5 Calculations for MS/MSD

12.2.5.1 Calculate the recovery of each Matrix Spike compound in the MS/MSD samples and report on the appropriate forms. Calculate the concentrations of the Matrix Spike compounds using the same equations as used for target compounds (Equations 5 and 6). Calculate the recovery of each Matrix Spike compound as follows:

EQ. 10 Matrix Spike Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample Result.

SR = Sample Result.

SA = Spike Added.

12.2.5.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the MS/MSD as follows:

EQ. 11 Relative Percent Difference Calculation

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative Percent Difference.

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

12.2.6 Technical Acceptance Criteria for MS/MSD

12.2.6.1 If requested, all MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2. All MS/MSDs must be analyzed on a GC/MS system meeting DFTPP, initial and continuing calibration verification technical acceptance criteria, and the method blank technical acceptance criteria. The MS/MSD must undergo cleanup procedures when required on a Gel Permeation Chromatograph (GPC) meeting the technical acceptance criteria for GPC calibration.

12.2.6.2 The MS/MSD must have an associated method blank meeting the blank technical acceptance criteria.

12.2.6.3 The MS/MSD must be extracted and analyzed within the contract holding time.

12.2.6.4 The RT shift for each of the internal standards must be within ±0.50 minutes (30 seconds) between the MS/MSD sample and the most recent opening CCV standard analysis.

12.2.6.5 The limits for Matrix Spike compound recovery and RPD are given in Table 5. As these limits are only advisory, no further action by the laboratory is required; however, frequent failure to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.2.7 Corrective Action for MS/MSD

Any MS/MSD that fails to meet the technical acceptance criteria in Sections 12.2.6.1, 12,2.6.2, 12.2.6.4, and 12.2.6.5 must be reanalyzed at no additional cost to USEPA. Only data from the MS/MSD that meets the technical acceptance criteria in Section 12.2.6 should be submitted.

12.3 Method Detection Limit (MDL) Determination

12.3.1 Before any field samples are analyzed under the contract, the MDL for each semivolatile target compound shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water, low-level soil and medium-level soils). The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), and GC column.

12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for water samples is achieved by analyzing a single reagent water blank (see method blank for water samples in Section 12.1) spiked with each semivolatile target compound at a concentration equal to two times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1.1. MDL verification for low-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for low-level soil samples in Section 12.1) spiked with each semivolatile target compound at a concentration equal to 1-4 times the analytically determined MDL. MDL verification for medium-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for medium-level soil samples in Section 12.1) spiked with each semivolatile target compound at a concentration equal to two times the analytically determined MDL. Samples used for MDL determination and verification must be subjected to the same extraction and cleanup procedures used for field samples. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Sections 11.1.1 through 11.1.2.5.5.

12.3.3 The determined concentration of the MDL must be less than the CRQL.

12.3.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to Laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C. 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). SW-846 Method 8270C. Revision 3. December 1996.

16.2 US Environmental Protection Agency. Continuous Liquid-Liquid Extraction. SW-846 Method 3520C. Revision 3. December 1996.

16.3 US Environmental Protection Agency. Automated Soxhlet Extraction. SW-846 Method 3541. Revision 0. September 1994.

16.4 US Environmental Protection Agency. Pressurized Fluid Extraction (PFE). SW-846 Method 3545A. Revision 1. January 1998.

16.5 US Environmental Protection Agency. Ultrasonic Extraction. SW-846 Method 3550C. Revision 3. November 2000.

16.6 US Environmental Protection Agency. Silica Gel Cleanup. SW-846 Method 3630C. Revision 3. December 1996.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Decafluorotriphenylphosphine Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	10.0 - 80.0% of mass 198
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	10.0 - 80.0% of mass 198
197	Less than 2.0% of mass 198
198	Base peak 100% relative abundance (see Note)
199	5.0 - 9.0% of mass 198
275	10.0 - 60.0% of mass 198
365	Greater than 1.0% of mass 198
441	Present but less than mass 443
442	Greater than 50.0% but less than or equal to 100% of mass 198
443	15.0 - 24.0% of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be up to 100% that of m/z 198.

Table 2

Semivolatile Internal Standards With Corresponding
Target and Deuterated Monitoring Compounds Assigned for Quantitation

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Benzaldehyde Phenol Bis(2-chloroethyl) ether 2-Chlorophenol 2-Methylphenol 2,2'-Oxybis-(1-chloro-propane) Acetophenone 4-Methylphenol N-Nitroso-di-n-propylamine Hexachloroethane Phenol-d_5 (DMC) Bis(2-chloroethyl) ether-d_8 (DMC) 2-Chlorophenol-d_4 (DMC) 4-Methylphenol-d_8 (DMC)	Nitrobenzene Isophorone 2-Nitrophenol 2,4-Dimethylphenol Bis(2-chloroethoxy)methane 2,4-Dichlorophenol 4-Chloroaniline Hexachlorobutadiene Caprolactam 4-Chloro-3-methylphenol 2-Methylnaphthalene Naphthalene Nitrobenzene-d_5 (DMC) 2-Nitrophenol-d_4 (DMC) 2,4-Dichlorophenol-d_3 (DMC) 4-Chloroaniline-d_4 (DMC) 2-Methylnapthalene-d_{10} (SIM- DMC)	Hexachlorocyclopentadiene 2,4,6-Trichlorophenol 2,4,5-Trichlorophenol 2,3,4,6-Tetrachlorophenol 1,1'-Biphenyl 2-Chloronaphthalene 2-Nitroaniline Dimethylphthalate Acenaphthylene 3-Nitroaniline Acenaphthene 2,4-Dinitrophenol 4-Nitrophenol Dibenzofuran 2,4-Dinitrotoluene 2,6-Dinitrotoluene 1,2,4,5-Tetrachlorobenzene Diethylphthalate 4-Chlorophenyl-phenylether Fluorene 4-Nitroaniline Acenaphthylene-d_8 (DMC) 4-Nitrophenol-d_4 (DMC) Dimethylphthalate-d_6 (DMC) Fluorene-d_{10} (DMC)
Phenanthrene-d_{10}	**Chrysene-d_{12}**	**Perylene-d_{12}**
4,6-Dinitro-2-methylphenol *N*-Nitrosodiphenylamine 4-Bromophenyl-phenylether Hexachlorobenzene Atrazine Pentachlorophenol Phenanthrene Anthracene Carbazole Di-n-butylphthalate Fluoranthene 4,6-Dinitro-2-methylphenol-d_2 (DMC) Anthracene-d_{10} (DMC) Fluoranthene-d_{10} (SIM-DMC)	Pyrene Butylbenzylphthalate 3,3'-Dichlorobenzidine Benzo(a)anthracene Bis(2-ethylhexyl)phthalate Chrysene Pyrene-d_{10} (DMC)	Di-n-octylphthalate Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene Benzo(a)pyrene-d_{12} (DMC)

Table 3

Characteristic Ions for Semivolatile
Target Compounds, Deuterated Monitoring Compounds, and Internal Standards

Parameter	Primary Quantitation Ion	Secondary Ion(s)
Benzaldehyde	77	105, 106
Phenol	94	65, 66
Bis-(2-chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
2-Methylphenol	108	107
2,2'-Oxybis-(l-chloropropane)	45	77, 79
Acetophenone	105	77, 51
4-Methylphenol	108	107
N-Nitroso-di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
Bis-(2-chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
Caprolactam	113	55, 56
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
1,1'-Biphenyl	154	153, 76
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
1,2,4,5-Tetrachlorobenzene	216	214, 179, 108, 143, 218
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249

Table 3

Characteristic Ions for Semivolatile
Target Compounds, Deuterated Monitoring Compounds,
and Internal Standards (Con't)

Parameter	Primary Quantitation Ion	Secondary Ion(s)
Atrazine	200	173, 215
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Bis-(2-ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl phthalate	149	none
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenzo(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
2,3,4,6-Tetrachlorophenol	232	131, 230, 166, 234, 168
Deuterated Monitoring Compounds		
Phenol-d_5	99	71, 42
Bis-(2-chloroethyl)ether-d_8	67	99, 69
2-Chlorophenol-d_4	132	134, 68, 66
4-Methylphenol-d_8	113	115, 54
Nitrobenzene-d_5	128	82, 54
2-Nitrophenol-d_4	143	69, 41, 42
2,4-Dichlorophenol-d_3	165	167, 101
4-Chloroaniline-d_4	131	133, 69
Dimethylphthalate-d_6	166	78
Acenaphthylene-d_8	160	80, 158
4-Nitrophenol-d_4	143	113, 41, 42
Fluorene-d_{10}	176	174, 87, 86
4,6-Dinitro-2-methylphenol-d_2	200	170, 52
Anthracene-d_{10}	188	94, 80
Pyrene-d_{10}	212	106, 104
Benzo(a)pyrene-d_{12}	264	132, 118
Fluoranthene-d_{10} (SIM)	212	106,104
2-Methylnapthalene-d_{10} (SIM)	152	151

Table 3

Characteristic Ions for Semivolatile
Target Compounds, Deuterated Monitoring Compounds,
and Internal Standards (Con't)

Parameter	Primary Quantitation Ion	Secondary Ion(s)
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

Table 4

Relative Response Factor Criteria for Initial and Continuing Calibration Verification of Semivolatile Target Compounds and Deuterated Monitoring Compounds

Semivolatile Compounds	Minimum RRF	Maximum %RSD[1]	Maximum %Diff[1]
Benzaldehyde	0.010	40.0	±40.0
Phenol	0.800	20.0	±25.0
Bis(2-chloroethyl) ether	0.700	20.0	±25.0
2-Chlorophenol	0.800	20.0	±25.0
2-Methylphenol	0.700	20.0	±25.0
2,2'-Oxybis-(1-chloropropane)	0.010	40.0	±40.0
Acetophenone	0.010	40.0	±40.0
4-Methylphenol	0.600	20.0	±25.0
N-Nitroso-di-n-propylamine	O.500	20.0	±25.0
Hexachloroethane	0.300	20.0	±25.0
Nitrobenzene	0.200	20.0	±25.0
Isophorone	0.400	20.0	±25.0
2-Nitrophenol	0.100	20.0	±25.0
2,4-Dimethylphenol	O.200	20.0	±25.0
Bis(2-chloroethoxy) methane	0.300	20.0	±25.0
2,4-Dichlorophenol	0.200	20.0	±25.0
Naphthalene	0.700	20.0	±25.0
4-Chloroaniline	0.010	40.0	±40.0
Hexachlorobutadiene	0.010	40.0	±40.0
Caprolactam	0.010	40.0	±40.0
4-Chloro-3-methylphenol	0.200	20.0	±25.0
2-Methylnaphthalene	0.400	20.0	±25.0
Hexachlorocyclopentadiene	0.010	40.0	±40.0
2,4,6-Trichlorophenol	0.200	20.0	±25.0
2,4,5-Trichlorophenol	0.200	20.0	±25.0
1,1'-Biphenyl	0.010	40.0	±40.0
2-Chloronaphthalene	0.800	20.0	±25.0
2-Nitroaniline	0.010	40.0	±40.0
Dimethylphthalate	0.010	40.0	±40.0
2,6-Dinitrotoluene	0.200	20.0	±25.0
Acenaphthylene	0.900	20.0	±25.0
3-Nitroaniline	0.010	40.0	±40.0
Acenaphthene	0.900	20.0	±25.0
2,4-Dinitrophenol	0.010	40.0	±40.0
4-Nitrophenol	0.010	40.0	±40.0
Dibenzofuran	0.800	20.0	±25.0
2,4-Dinitrotoluene	0.200	20.0	±25.0
Diethylphthalate	0.010	40.0	±40.0
1,2,4,5-Tetrachlorobenzene	0.010	40.0	±40.0
4-Chlorophenyl-phenylether	0.400	20.0	±25.0
Fluorene	0.900	20.0	±25.0
4-Nitroaniline	0.010	40.0	±40.0
4,6-Dinitro-2-methylphenol	0.010	40.0	±40.0
4-Bromophenyl-phenyl ether	0.100	20.0	±25.0
N-Nitrosodiphenylamine	0.010	40.0	±40.0
Hexachlorobenzene	0.100	20.0	±25.0

Table 4

Relative Response Factor Criteria for Initial and Continuing Calibration Verification of Semivolatile Target Compounds and Deuterated Monitoring Compounds (Con't)

Semivolatile Compounds	Minimum RRF	Maximum %RSD[1]	Maximum %Diff[1]
Atrazine	0.010	40.0	±40.0
Pentachlorophenol	0.050	20.0	±25.0
Phenanthrene	0.700	20.0	±25.0
Anthracene	0.700	20.0	±25.0
Carbazole	0.010	40.0	±40.0
Di-n-butylphthalate	0.010	40.0	±40.0
Fluoranthene	0.600	20.0	±25.0
Pyrene	0.600	20.0	±25.0
Butylbenzylphthalate	0.010	40.0	±40.0
3,3'-Dichlorobenzidine	0.010	40.0	±40.0
Benzo(a)anthracene	0.800	20.0	±25.0
Chrysene	0.700	20.0	±25.0
Bis-(2-ethylhexyl)phthalate	0.010	40.0	±40.0
Di-n-octylphthalate	0.010	40.0	±40.0
Benzo(b)fluoranthene	0.700	20.0	±25.0
Benzo(k)fluoranthene	0.700	20.0	±25.0
Benzo(a)pyrene	0.700	20.0	±25.0
Indeno(1,2,3-cd)pyrene	0.500	20.0	±25.0
Dibenzo(a,h)anthracene	0.400	20.0	±25.0
Benzo(g,h,i)perylene	0.500	20.0	±25.0
2,3,4,6-Tetrachlorophenol	0.100	20.0	±25.0
Deuterated Monitoring Compounds			
Phenol-d_5	0.010	20.0	±25.0
Bis-(2-chloroethyl)ether-d_8	0.010	20.0	±25.0
2-Chlorophenol-d_4	0.010	20.0	±25.0
4-Methylphenol-d_8	0.010	20.0	±25.0
Nitrobenzene-d_5	0.010	20.0	±25.0
2-Nitrophenol-d_4	0.010	20.0	±25.0
2,4-Dichlorophenol-d_3	0.010	20.0	±25.0
4-Chloroaniline-d_4	0.010	40.0	±40.0
Dimethylphthalate-d_6	0.010	40.0	±40.0
Acenaphthylene-d_8	0.010	20.0	±25.0
4-Nitrophenol-d_4	0.010	40.0	±40.0
Fluorene-d_{10}	0.010	20.0	±25.0
4,6-Dinitro-2-methylphenol-d_2	0.010	40.0	±40.0
Anthracene-d_{10}	0.010	20.0	±25.0
Pyrene-d_{10}	0.010	20.0	±25.0
Benzo(a)pyrene-d_{12}	0.010	20.0	±25.0
Fluoranthene-d_{10} (SIM)	0.010	20.0	±25.0
2-Methylnapthalene-d_{10} (SIM)	0.010	20.0	±25.0

[1] For a closing CCV, all target compounds and DMCs must meet a minimum RRF of 0.010 and a maximum % Difference of ±50.0.

Table 5

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	%Recovery Water	RPD Water	%Recovery Soil/Sediment	RPD Soil/Sediment
Phenol	12-110	0-42	26-90	0-35
2-Chlorophenol	27-123	0-40	25-102	0-50
N-Nitroso-di-n-propylamine	41-116	0-38	41-126	0-38
4-Chloro-3-methylphenol	23-97	0-42	26-103	0-33
Acenaphthene	46-118	0-31	31-137	0-19
4-Nitrophenol	10-80	0-50	11-114	0-50
2,4-Dinitrotoluene	24-96	0-38	28-89	0-47
Pentachlorophenol	9-103	0-50	17-109	0-47
Pyrene	26-127	0-31	35-142	0-36

Table 6

Deuterated Monitoring Compound Recovery Limits

Compound	% Recovery For Water Samples	% Recovery For Soil Samples
Phenol-d_5	39-106	17-103
Bis-(2-chloroethyl)ether-d_8	40-105	12-98
2-Chlorophenol-d_4	41-106	13-101
4-Methylphenol-d_8	25-111	8-100
Nitrobenzene-d_5	43-108	16-103
2-Nitrophenol-d_4	40-108	16-104
2,4-Dichlorophenol-d_3	37-105	23-104
4-Chloroaniline-d_4	1-145	1-145
Dimethylphthalate-d_6	47-114	43-111
Acenaphthylene-d_8	41-107	20-97
4-Nitrophenol-d_4	33-116	16-166
Fluorene-d_{10}	42-111	40-108
4,6-Dinitro-2-methylphenol-d_2	22-104	1-121
Anthracene-d_{10}	44-110	22-98
Pyrene-d_{10}	52-119	51-120
Benzo(a)pyrene-d_{12}	32-121	43-111
Fluoranthene-d_{10} (SIM)	50-150	50-150
2-Methylnapthalene-d_{10} (SIM)	50-150	50-150

Table 7

Semivolatile Deuterated Monitoring Compounds
and the Associated Target Compounds

Phenol-d_5 (DMC)	**2-Chlorophenol-d_4 (DMC)**	**2-Nitrophenol-d_4**
Benzaldehyde	2-Chlorophenol	Isophorone
Phenol		2-Nitrophenol

bis(2-Chloroethyl) ether-d_8 (DMC)	**4-Methylphenol-d_8 (DMC)**	**4-Chloroaniline-d_4 (DMC)**
bis(2-Chloroethyl) ether	2-Methylphenol	4-Chloroaniline
2,2'-oxybis(1-Chloropropane)	4-Methylphenol	Hexachlorocyclopentadiene
bis(2-Chloroethoxy) methane	2,4-Dimethylphenol	3,3'-Dichlorobenzidine

Nitrobenzene-d_5 (DMC)	**2,4-Dichlorophenol-d_3 (DMC)**	**Dimethylphthalate-d_6 (DMC)**
Acetophenone	2,4-Dichlorophenol	Caprolactam
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	1,1'-Biphenyl
Hexachloroethane	4-Chloro-3-methylphenol	Dimethylphthalate
Nitrobenzene	2,4,6-Trichlorophenol	Diethylphthalate
2,6-Dinitrotoluene	2,4,5-Trichlorophenol	Di-n-butylphthalate
2,4-Dinitrotoluene	1,2,4,5-Tetrachlorobenzene	Butylbenzylphthalate
N-Nitrosodiphenylamine	Pentachlorophenol	bis(2-Ethylhexyl) phthalate
	2,3,4,6-Tetrachlorophenol	Di-n-octylphthalate

Fluorene-d_{10} (DMC)	**Anthracene-d_{10} (DMC)**	**Pyrene-d_{10} (DMC)**
Dibenzofuran	Hexachlorobenzene	Fluoranthene
Fluorene	Atrazine	Pyrene
4-Chlorophenyl-phenylether	Phenanthrene	Benzo(a)anthracene
4-Bromophenyl-phenylether	Anthracene	Chrysene
Carbazole		

Acenaphthylene-d_8 (DMC)	**4-Nitrophenol-d_4**	**Benzo (a) pyrene-d_{12} (DMC)**
Naphthalene	2-Nitroaniline	Benzo(b)fluoranthene
2-Methylnaphthalene	3-Nitroaniline	Benzo(k)fluoranthene
2-Chloronaphthalene	2,4-Dinitrophenol	Benzo(a)pyrene
Acenaphthylene	4-Nitrophenol	Indeno(1,2,3-cd)pyrene
Acenaphthene	4-Nitroaniline	Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene

4,6-Dinitro-2-methylphenol-d_2 (DMC)
4,6-Dinitro-2-methylphenol

Table 8

Semivolatile Deuterated Monitoring Compounds and the Associated Target Compounds for Selected Ion Monitoring Analysis

Fluoranthene-d_{10}	**2-Methylnaphthalene-d_{10}**
Fluoranthene	Napthalene
Pyrene	2-Methylnaphthalene
Benzo(a)anthracene	Acenapthylene
Chrysene	Acenaphthene
Benzo(b)fluoranthene	Fluorene
Benzo(k)fluoranthene	Pentachlorophenol
Benzo(a)pyrene	Phenanthrene
Indeno(1,2,3-cd)pyrene	Anthracene
Dibenzo(a,h)anthracene	
Benzo(g,h,i)perylene	